(11) EP 1 294 035 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 19.03.2003 Bulletin 2003/12

(51) Int CI.7: **H01M 8/02**, H01M 8/24

(21) Application number: 02256336.5

(22) Date of filing: 12.09.2002

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR
Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 13.09.2001 JP 2001278076 23.10.2001 JP 2001324603 13.06.2002 JP 2002172368 13.06.2002 JP 2002172673

(71) Applicant: NGK INSULATORS, LTD.
Nagoya-City, Aichi Prefecture 467-8530 (JP)

(72) Inventors:

 Ito, S., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)

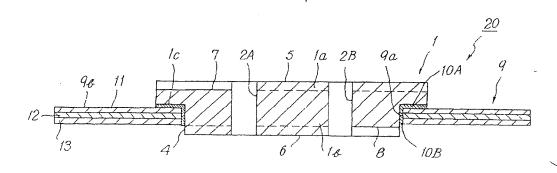
- Ryu, T., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)
- Shimizu, S., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)
- Okumura, K., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)
- Hattori, M., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)
- (74) Representative: Paget, Hugh Charles Edward et al MEWBURN ELLIS York House
 23 Kingsway
 London WC2B 6HP (GB)

from KYP-100-A

- (54) A holding member for holding an electrochemical cell, a holding structure for the same, an electrochemical system and a connecting member for electrochemical cells
- (57) The invention provides an assembly structure for facilitating the assembly of laminated single cells, for reducing the possibility of gas leakage after repeated cycles of temperature elevation and reduction, and for preventing the reduction of working efficiency of cells due to the gas leakage. A plate-shaped electrochemical cell 9 made of a ceramic material with a through hole 9a formed therein is held by a holding member 1. The mem-

ber 1 is made of a ceramic material and has a plate-shaped main body 1a of a shape of a flat plate and a protruded portion 1b protruding from the main body 1a. A first supply hole 2A for supplying one gas and a second supply hole 2B for supplying the other gas are formed in the holding member 1. The main body 1a has a sealing surface 1c against the one main face 9a of the cell 9 while the protruded portion 1b is inserted into the through hole 9a.

Fig. 4



of thermal expansion after repeated thermal cycles of temperature elevation and reduction. The gas leakage may be likely to increase as a result.

[0011] Further in a prior planar type solid oxide fuel cell, gas sealing is assured in the outer boundary of the planar type fuel cell structure. It is thus difficult to reduce the thermal stress generated in the central portion of the cell so that the cell might be susceptible to crack formation.

[0012] Further, when nickel felt is used as an electrically conductive connecting member, a fuel gas may be supplied into small gaps within the nickel felt and remains in it, and then it may be discharged outside of a container before contributing to power generation. When hydrogen is used as the fuel gas, the power generation causes water production on a anode electrode side. However, the produced water may be advanced into small gaps within the nickel felt and remain therein. In this case, the partial pressure of oxygen in fuel gas is increased as a result of the chemical equilibrium of water-oxygen-hydrogen system in the fuel gas, resulting in a decrease of the open circuit voltage. Further, mechanical pressing on the cell is needed to reduce the contact resistance and thus to improve the electrical connection. In this case, the electrochemical cell might be susceptible to crack formation.

[0013] An object of the invention is to provide a novel electrochemical system having a planar single cells stacked with each other, and to facilitate the stacking of the single cells and separator.

[0014] Another object of the invention is to reduce the possibility of gas leakage after repeated cycles of temperature elevation and reduction and to prevent the reduction of generating efficiency of the cells due to the gas leakage.

[0015] When a mesh is used as an electrically conductive connecting member, a fuel gas flows within grooves of the separator and is supplied onto an electrode surface. In this case, since metallic wire of the mesh contacts and covers the electrode surface, the fuel gas cannot be supplied onto the electrode surface at parts covered with the metallic wire and is lost. Further, although the fuel gas can be supplied within grooves on the separator, the fuel gas is not penetrated to a part of a protrusion in the separator as will be described later. This is because, a mesh is sandwiched and pressed between a surface of the protrusion and the electrode surface, the mesh (metallic wire forming the mesh) works as an obstacle for the supplying fuel gas. The penetration of a fuel gas into gaps (interstices) between the protrusion surface and electrode surface is thus prevented. As a result, a substantial area in the electrode surface of a single cell does not contribute to power generation. Further, when a mesh is sandwiched between the protrusion surface and the electrode surface and pressed, the deformation of the mesh in the thickness direction is relatively small. In this case, one side or uneven pressing on an electrochemical cell is likely to occur due

to a slight distortion in the cell, thereby the cell might be susceptible to crack formation.

[0016] Further, when a corrugated metallic sheet, for example an expanded metal is used as an electrically conductive connecting member, the stacking and pressing of the electrically conductive connecting member and the separator caused the following problems. That is, when a plurality of corrugated sheets and separators are alternately stacked to form a generator, this stack are pressurized toward the stacking direction by a given pressing mechanism. By this pressing the corrugated sheet is compression-deformed in such a manner that the thickness of the corrugated sheet is reduced. In this case, if the pressing direction is perfectly controlled to the stacking direction, there is no problem. Nevertheless, in practice a correct control of the pressing direction is difficult.

[0017] For example, as shown in FIG. 1(a), a corrugated sheet 82 is sandwiched between an electrochemical cell 81 and a separator 80 and is pressed. In this case, it is common that the centers of gravity of respective loads in both ends (upper and lower ends) of the stack are slightly shifted. Namely, in this case, a load is applied toward slanted directions S and T with respect to the stacking direction A on a corrugated sheet, as shown by an arrow R. As a result, a pressure perpendicular to the stacking direction A is applied onto the corrugated sheet 82. Wen a pressure in a direction of an arrow T is applied as shown in FIG. 1 (b), the deformation of the corrugated sheet 82 is small. However, if a component of the direction of an arrow S is present in a pressure on the sheet, the entire corrugated sheet 82 is deformed in such a manner that it is crushed toward the corrugation advancing direction (direction of an arrow S). As a result, the separator 80 and the electrochemical cell 81 are shifted in the direction of arrow S so that the assembled cells may be broken.

[0018] An object of the present invention is to provide a novel electrochemical system with an electrochemical cell and an electrically conductive connecting member contacting the cell, and to prevent the residence of a gas within the connecting member.

[0019] Another object of the present invention is to reduce a region on an electrode surface of the electrochemical cell which is not in contact with a gas.

[0020] Still another object of the present invention is to reduce the contact resistance of the connecting member, so that soft contact of the connecting member and the cell may be realized and the breakage of the cell may be prevented.

(Disclosure of a first aspect of the invention)

[0021] A first aspect of the present invention provides a holding member having one and the other main faces for holding a planar electrochemical cell, The cell is made of a ceramic material with a through hole formed therein. The holding member is made of a ceramic ma-

50

as an electrically conductive connecting member according to one embodiment of the present invention.

[0040] FIG. 11 is a cross-sectional view showing a part of the mesh 31 in FIG. 10 in an enlarged scale.

[0041] FIG. 12 is a principal cross-sectional view showing a state where the mesh 31 was intervened between a separator 37 and an electrochemical cell 38.

[0042] FIG. 13 is a principal cross-sectional view showing a state where non-emboss shape provided mesh 41 was intervened between the separator 37 and the electrochemical cell 38.

[0043] FIG. 14 is a cross-sectional view showing a part of a mesh 51 according to another embodiment of the present invention.

[0044] FIG. 15 is a principal cross-sectional view showing a state where a mesh 51 was intervened between the separator 37 and the electrochemical cell 38.

[0045] FIG. 16 is a perspective view showing an electrically conductive connecting member 61 consisting of a punching metal.

[0046] FIG. 17 is a perspective view showing an electrically conductive connecting member 71 consisting of an expanded metal.

[0047] FIG. 18 (a) is a plan view showing a separator 65A.

[0048] FIG. 18 (b) is a cross-sectional view taken along a line XVIIIb - XVIIIb of the separator 65A.

[0049] FIG. 19 (a) is a plan view showing a separator 65B.

[0050] FIG. 19 (b) is a cross-sectional view taken along a line XVIVb - XVIVb of the separator 65B.

[0051] FIG. 20 (a) is a plan view showing a separator 65C.

[0052] FIG. 20 (b) is a cross-sectional view taken along a line XXb - XXb of the separator 65C.

[0053] FIG. 21 (a) is a plan view showing a separator 65D when viewed from the main surface 65b side thereof

[0054] FIG. 21 (b) is a cross-sectional view taken along a line XXIb - XXIb of the separator 65D.

[0055] FIG. 22 is a plan view of the separator 65D when viewed from the main surface 65a side thereof.

[0056] FIG. 23 is a schematic view showing an experimental device for power generation tests.

Preferred embodiments of the invention

(Detailed description of the first aspect of the present invention)

[0057] The first aspect of the present invention, especially the adventages, effects and preferred embodiments, will be described below, referring to the attached drawings.

[0058] FIG. 2 is a cross-sectional view schematically showing a holding member 1 according to one embodiment of the first aspect of the invention. FIG. 3 (a) is a plan view of the holding member 1 when viewed from

the main surface 5 side, and FIG. 3 (b) is a plan view of the holding member 1 when viewed from the main surface 6 side.

[0059] Although the planar shape of the holding member 1 is substantially round as shown, for example, in FIG. 3, the shape is not limited to the round shape, but an oval shape, or a polygonal shape may be used. For minimizing the thermal stress in the single cell, the holding member 1 is preferably substantially round. The holding member 1 has a main body 1a having a comparatively larger diameter and a protruded portion 1b having a comparatively smaller diameter. Further, a pair of through holes 2A and 2B are formed between the main surfaces 5 and 6 so that they penetrate the main body 1a and protruded portion 1b. The through hole 2A is a supply hole for one gas and the through hole 2B is a supply hole for the other gas. The reference numerals 5 and 6 each denotes a sealing surface against the adjacent separators as will be described later, and each sealing face is flat in the present example. The reference numerals 1c and 4 each denotes a sealing surface against an electrochemical cell, as described later.

[0060] One gas passage 7 is formed on the main surface 5 side of the main body 1a, and the other gas passage 8 is formed on the main surface 6 side of the protruded portion 1b. The passage 7 is composed of a groove formed on the side of the main surface 5, as shown in FIG. 3 (a) and communicates with one supply hole 2A. The flow passage 8 is composed of a groove formed on the side of the main surface 6, as shown in FIG. 3 (b) and communicates with the other supply hole 2B.

[0061] FIG. 4 is a holding structure 20 comprising an electrochemical cell 9 and a holding member 1 holding the cell. The cell 9 is formed of a three-layered structure comprising, for example, one electrode 11, a solid electrolyte layer 12 and the other electrode 13. A protruded portion 1b is inserted through a through hole 9a of the cell 9. A sealing member 10B is intervened between the outer peripheral surface 4 of the protruded portion 1b and the cell 9. Further, a sealing member 10A is intervened between the one main surface 9b of the cell 9 and the sealing face 1c of a flange portion of the main body 1a.

[0062] FIG. 5 is a cross-sectional view showing a planar separator 15 stacked on the holding structure 20 in FIG. 4. Further, FIG. 6 is a schematic cross-sectional view showing an electrochemical system obtained by stacking the holding structures 20 and the separators 15 shown in FIG. 5. In FIG. 5, only three layers of electrochemical cells and separators are drawn because of the limitation of the drawing sheet, but the numbers of the cells and separators can be optionally changed.

[0063] In this example, the separator 15 is flat plateshaped and is made of an electrically conductive material such as a metal or the like. In the separator 15, a pair of through holes 16A and 16B are formed at positions corresponding to the through holes 2A and 2B of

50

gas passage in the holding member so as to prevent the reduction in strength of the holding member around the sealing surface.

[0075] It is thus preferred to shift at least a part of the function of gas supply passage to the separator by providing a gas supply passage in the separator, for ensuring the mechanical strength of the ceramic holding member under heating and pressing.

[0076] Thus, in a preferred embodiment, the separator is provided with one supply passage communicating with one gas supply hole of the holding member and a space over the electrochemical cell. In this case, since a part of the function of gas supply is transferred to the separator, the one gas passage in the holding member may be reduced or may be omitted. Accordingly, the mechanical stability near the sealing surface of the holding member may be improved. Most preferably, the holding member is not provided with the one gas passage.

[0077] In a preferred embodiment, the separator is provided with the other supply passage communicating with the other gas supply hole and a space over the electrochemical cell. In this case, the other gas passage in the holding member may be also reduced or omitted. Most preferably, the holding member is not provided with the other gas passage.

[0078] The material for a separator is not particularly limited, as far as the material is resistive against a gas used at an operating temperature. The separator may preferably be, for example, a complex oxide of perovskite type containing lanthanum and more preferably be lanthanum chromite.

[0079] The separator may preferably be made of a metal such as stainless steel, a nickel-based alloy, a co-balt-based alloy and an iron-based alloy. In this case, gas supply passage having various shapes may be formed in the separator. Further, the separator is unlikely to break under heating and pressing.

[0080] FIGS. 7 to 9 show an electrochemical system according to such embodiment. FIG. 7 is a cross-sectional view showing a separator 15A. The separator 15A is substantially flat plate-shaped as a whole. The separator 15A is provided with gas supply holes 15c and 15d communicating with the corresponding supply holes of the holding member, and is also provided with gas supply passage 15e and 15f. Each of the gas supply passage 15e and 15f has a portion extending in substantially parallel with the direction of an arrow A and a portion extending substantially vertical thereto, so that each passage is bent. Further, the separator 15A is provided with recess 15h and 15g for receiving the respective sealing members.

[0081] In a preferred embodiment, the gas supply passage formed in the separator may be bent and/or curved. Such design is effective for diffusing the gas radially at the outer periphery of the holding member just before entering the power generating room, and for supplying the gas uniformly onto the whole surface of the cell.

[0082] As shown in FIG. 8, the holding structure 20A. the separator 15A and sealing member 17 are laid alternately to prepare a stack. In the present example, the holding member 1A does not include such a gas supply passage communicating with the space 19 or 29. The respective sealing members 17 are received in the recess 15g and 15h and thus fixed. One gas flows in a gas supply hole 16A as an arrow B, and then flows in the gas supply passage 15e in the separator 15A while being bent as an arrow E, and then is supplied into the space 19. The other gas flows in a gas supply hole 16B as an arrow D, and then flows in the gas supply passage 15f in the separator 15A while being bent as an arrow F, and then is supplied into the space 29. When the gas flows in bent supply passage 15e and 15f, the gas is diffused radially at the outer periphery of the holding member just after supplied into the space 19 and 29. The diffused gas may thus be supplied into the spaces 19 and 29 uniformly. Accordingly, the use efficiency of gas is enhanced. The gas supply passage may be bent two or more times. The separator surfaces 15a and 15b directly facing the spaces 19 and 29, respectively, may be provided with a gas flow passage with an uneven shape. As a result, the flow of supplied gas is controlled by the passage, so that the gas may be uniformly supplied into the whole of the spaces.

[0083] In a preferred embodiment, an assembled generator is produced by a plurality of separators, electrochemical cells and holding members, and a holding structure for holding the assembled cell while pressing them is provided. This pressing mechanism is not particularly limited. For example, this pressing mechanism may be a fastening member such as a bolt or the like, or a pressing mechanism such as a spring or the like.

[0084] FIG. 9 is a schematic view showing an assembled generator according to the present embodiment. An assembled generator (stack) 28 is formed by stacking and assembling the above-mentioned separators 15A, the holding members 1A, the electrochemical cells 9 and connecting members. Pressing plates 23A and 23B are located at the upper and lower ends of this assembled generator 28, respectively, and they sandwich the generator 28. The pressing plates 23A and 23B are fastened by a fastening mechanism 24 and pressed by a bolt (a fastening mechanism), in a direction of an arrow .A. To the gas supply holes 16A and 16B are connected exterior gas pipes 26 and 25, respectively, so that gas can be supplied. The connection of this gas pipe to the gas supply hole is not limited. For example, the gas pipes may be connected to both of the upper and lower ends of the stack, respectively, so that one gas flows from the upper to the lower ends and the other gas flows from the lower to upper ends. Such design may be effective for supplying gas uniformly to the generator (stack).

[0085] As described above, according to the first aspect of the present invention, it is possible to facilitate the assembly and stacking of single cells, to reduce the

total of a width "d" of the non emboss shape provided portion 31a and a height "h" of the emboss shape provided portion 31b of the mesh, as shown in FIG. 11.

[0094] By such structure, the one gas flows within the passage 43A and, at the same time, flows within the passage 43B formed by the mesh 31 and the separator 37 as shown by an arrow K. One gas then contacts one electrode 39 through the mesh interstices 33 in the nonemboss shape provided portion 31a from the space 43B as shown by an arrow M. At the same time, the gas flowing in the space 43B is passed through the mesh interstices 33A in the emboss shape provided portion 31b, as shown by an arrow L. The gas then flows into the flow passage 43C (space 35) between the emboss shape provided portion 31b and the one electrode 39, so that the gas contacts the one electrode 39 within the flow passage 43C.

[0095] On the other hand, when emboss shape provided portions are not provided in the mesh, the mesh 41 braided flatly is sandwiched between the separator 37 and cell 38, as shown in FIG. 13. One side 41c of the mesh 41 contacts a protruded surface 37b of the separator 37. The other side 41d of the mesh 41 contacts a surface of the one electrode 39. When gas is supplied to the passage 43A in this state, this gas contacts the one electrode 39 as shown by an arrow N from the passage 43A. However, the mesh interstices 43D between the protruded surface 37b and the electrode 39 is surrounded by an electrically conductive wires 42. That is, the electrically conductive wires 42 block the flow of gas from the passage 43A into a gap 43D between the protruded surface 37b and the electrode 39. Thus, in the area of the passage 43A (groove 37a), gas can be supplied to the electrode of the electrochemical cell. However, in the area of the protruded surface 37b, gas is hardly supplied to the electrode.

[0096] Further, even when the pressing direction for the assembled cells is slanted from the stacking direction A in the present invention, the emboss shape provided portions are flatly and regularly formed as shown in FIG. 10. It is thus possible to prevent the crush of the mesh in a specific direction and the lateral shift of the separator and electrochemical cell.

[0097] The material for the connecting member according to the second aspect must be stable with respect to a gas to which this member is exposed, at an operating temperature of an electrochemical cell. Specifically, materials stable against an oxidizing gas include platinum, silver, gold, palladium, a nickel-based alloy such as Inconel, nichrom and the like, a cobalt-based alloy such as Haynes alloy and the like, and an iron-based alloy such as stainless steel and the like. Materials which are stable against a reducing gas include nickel and nickel-based alloy in addition to the above described materials stable against an oxidizing gas.

[0098] An emboss shape provided portion means a portion having an optional shape obtained by a plastic deformation process such as embossing. The process

for imparting an emboss shape may be any forming process for press-deforming a part of a permeable member such as a mesh to form the above-mentioned protruded portion (embossed portion) and a recess 35. The concrete performance process is not limited. Typically, the emboss shape may be provided by pressing the permeable member such as a mesh with an embossing die, such as a deep drawing process or the like. [0099] A permeable material forming a connecting member is not limited, as far as it has permeability. However, preferably it can be plastically deformed during pressing. The permeable materials are preferably as follows.

Mesh (mesh-like object)

[0100] Metallic plate in which a large number of vent holes are regularly formed: Preferably, a punching metal, an etching metal, an expanded metal (expand)

[0101] It is preferred that the emboss shape provided portions are regularly formed in plan view. It is particularly preferable that the emboss shape provided portions are arranged in at least two directions in plan view. [0102] In a permeable material (for example a mesh) forming a connecting member, the height h (see FIG. 11) of the emboss shape provided portion from the nonemboss shape provided portion is not particularly limited. However, from the viewpoint of improving the gas flow, the height is preferably 0.3 mm or more, and more preferably 0.5 mm or more. However, when the height h is too large, the volume of a space for the gas flow is increased. Thus, the volume of an useless gas, which is not utilized by the cell and is passed there through, is possibly increased and the generating efficiency of the cell per an unit volume is possibly reduced. From this viewpoint, the height h is preferably 5 mm or less and more preferably 3 mm or less.

[0103] The dimension of each emboss shape provided portion, the number of the portions and the planar shape of the portion are not particularly limited, and a round circular shape, an oval shape, a triangular shape, a rectangular shape, and a hexagonal shape in a plan view may be used.

[0104] In a preferred embodiment, the emboss shape provided portion comprises a first emboss shape provided portion protruded on one surface side of the permeable material, and a second emboss shape provided portion protruded on the other surface side of the permeable material. Accordingly, the pressure loss of gas flow can be further reduced. FIGS. 14 and 15 shows this embodiment. FIG. 14 is a part of cross-sectional view of a mesh 51, and FIG. 15 shows a state where the mesh 51 is sandwiched between an electrochemical cell 38 and a separator 37.

[0105] The planar shape of the mesh 51 is for example circular. The mesh 51 can be obtained by braiding a large number of electrically conductive wires 32. Between the large number of electrically conductive wires

65A, and FIG. 18 (b) is a cross-sectional view taken along a line XVIIIb - XVIIIb of the separator 65A. The separator 65A includes gas supply holes 65c and 65d, and each gas supply hole communicates with a gas supply hole of an electrochemical cell not shown, as described above. Further, each gas supply hole communicates with a substantially circular recess 65e and it functions as a receiving portion for a sealing member. Further, the gas supply hole 65c is provided with elongated gas distribution grooves 65g and 65h as gas supply passages. On the main surface 65b side of the separator 65A is formed a recess 65f substantially all over the separator surface. Each of the gas distribution grooves 65g and 65h communicates with the recess 65f. The recess 65f functions as a receiving portion for a connecting member, and has an effect to allow gas to diffuse to the entire surface of the separator 65A.

[0119] One gas or the other gas flows in the gas supply hole 65c. penetrates through the gas distribution grooves 65g and 65h, and then flows over the surface of a ring-shaped gas distributing recess 65f. A gas flow passage may be formed in the recess 65f. The main surface 65b of the separator 65A is opposite to an electrode of the electrochemical cell, as described above.

[0120] FIG. 19 (a) is a plan view showing a separator 65B, and FIG. 19 (b) is a cross-sectional view taken along a line XVIVb - XVIVb of the separator 65B. The separator 65B is further provided with an elongated gas distribution groove 65j communicating with the gas supply hole 65c.

[0121] FIG. 20 (a) is a plan view showing a separator 65C, and FIG. 20 (b) is a cross-sectional view taken along a line XXb - XXb of the separator 65C. The separator 65C is not provided with an elongated gas distribution groove in an recess 65e, and instead is provided with an arc-shaped gas distribution groove 65k.

[0122] In each of separators of FIGS. 18 to 20, a gas distribution groove for either of one gas and the other gas is provided in the separator. However, the gas distribution grooves for both gases can be provided in the sides of one and the other main faces of the separator, respectively. FIGS. 21 and 22 relate to this embodiment. [0123] FIG. 21 (a) is a plan view of a separator 65D when viewed from the main surface 65b side, and FIG. 21 (b) is a cross-sectional view of the separator 65D taken along a line XXIb - XXIb thereof. FIG. 22 is a plan view of the separator 65D when viewed from the main surface 65a side.

[0124] The separator 65D is provided with gas supply holes 65c and 65d, and each gas supply hole communicates with a gas supply hole of an electrochemical cell not shown, as described above. Further, each gas supply hole communicates with a substantially circular recess 65e on the main surface 65b side and also communicates with a substantially circular recess 65p on the main surface 65a side. The respective recess portions 65e and 65p function as receiving portions for the sealing members, respectively. Further, the inside of the re-

cess 65e is provided with elongated gas distribution grooves 65g and 65h as the gas supply passages. Also, the inside of the recess portion 65p is provided with elongated gas distribution grooves 65m and 65n as the gas supply passages.

[0125] One gas flows through the gas supply hole 65c, and then is passed through the gas distribution grooves 65g and 65h, so that it flows through a space between the separator 65D and the electrochemical cell. The other gas flows through the gas supply hole 65d, and then passed through the gas distribution grooves 65m and 65n, so that it flows through a space between the separator 65D and the electrochemical cell

(Description of preferred embodiments of the first and second aspects of the present invention)

[0126] Preferred embodiments common for the first and second aspects will be described below.

[0127] In a preferred embodiment, one gas is an oxidizing gas and the other gas is a reducing gas.

[0128] The oxidizing gas is not particularly limited, as far as oxygen ions may be supplied to a solid electrolyte film from the gas. The gas includes air, diluted air, oxygen and diluted oxygen.

[0129] The reducing gas includes hydrogen, carbon monooxide, methane or the mixture thereof.

[0130] An electrochemical cell means a cell performing an electrochemical reaction, in the invention.

[0131] For example, an electrochemical cell includes an oxygen pump and a high temperature vapor electrolyte cell. The high temperature vapor electrolyte cell can be used as a hydrogen production device, and also as a removing system of water vapor. Further, the electrochemical cell can be used as a decomposition cell for NO_X and/or SO_X. This Decomposition cell can be use as a purification apparatus for discharge gas from motor vehicles, power generation devices or the like. In this case, oxygen in the discharge gas is removed through a solid electrolyte film while NO_X is electrolyzed into nitrogen and oxygen, and the oxygen thus produced by this decomposition can be also removed. Further, by this process, vapor in the discharge gas is electrolyzed to produce hydrogen and oxygen, and the produced hydrogen reduces NO_X to N₂. Further, in a preferable embodiment, the electrochemical cell is a solid oxide fuelcell.

[0132] The one electrode and the other electrode each may be a cathode or an anode.

[0133] The material for a solid electrolyte layer is not limited particularly, and may be yttria-stabilized zirconia or yttria partially-stabilized zirconia. In the case of NO_X decomposition cell, cerium oxide is also preferable.

[0134] The cathode material is preferably lanthanumcontaining perovskite-type complex oxide, more preferably lanthanum manganite or lanthanum cobaltite, and most preferably lanthanum manganite. Into lanthanum

10

20

40

45

with a punch having a diameter of 3 mm. Thus, an uneven cross-sectional shape was provided to the mesh as shown in FIG. 5.

(Power generation test)

[0146] FIG. 22 shows a state where a mesh 51 is sandwiched between an electrochemical cell 38 and a separator 37 in a power generation device and is loaded in a direction A. The electrochemical cell assembled as shown in FIG. 22 was set in an electric furnace. While allowing argon gas to pass on a reducing side and air to pass on an oxidizing side, the furnace was heated to 800 °C and argon was substituted with hydrogen on the reducing side. Then while allowing air of 1 L/min and hydrogen of 1 L/min to flow, current-voltage properties were measured, whereby a maximum power of 0.2 W/ cm² was obtained. After the measuring no breakage of the cell was observed. In comparison with it, non-emboss shape-formed 200 mesh stainless steel mesh was substituted for the mesh 51 and the current-voltage properties were measured. A maximum power of 0.05 W/cm² was obtained.

[0147] The present invention has been explained referring to the preferred embodiments, however, the present invention is not limited to the illustrated embodiments which are given by way of examples only, and may be carried out in various modes without departing from the scope of the invention.

Claims

A holding member for holding a planar electrochemical cell having one and the other main faces, said cell being made of a ceramic material with a through hole formed therein:

wherein said holding member is made of a ceramic material and comprises a planar main body, a protruded portion protruding from said main body, a first supply hole for supplying one gas formed therein and a second supply hole for supplying the other gas formed therein, and said main body has a sealing surface against said one main face of said cell while said protruded portion is inserted into said through hole.

- 2. The member of claim 1, wherein said main body comprises a gas passage communicating with said first supply hole and a space over said cell.
- The member of claim 1 or 2, wherein said protruded portion comprises a gas passage communicating with said second supply hole and a space over said cell.
- The member of any one of claims 1 to 3, comprising an additional sealing surface against an separator

connecting a plurality of said cells.

5. An electrochemical system comprising a plurality of planar electrochemical cells each having one and the other main faces, a holding member for holding said cell, and a separator electrically connecting said cells with each other:

wherein said cell is made of a ceramic material with a through hole formed therein, said separator and said cells are stacked alternately, said holding member is made of a ceramic material, said holding member comprises a planar main body, a protruded portion protruding from said main body, a first supply hole for supplying one gas formed therein and a second supply hole for supplying the other gas formed therein, and said main body has a sealing surface against said one main face of said cell while said protruded portion is inserted into said through hole.

- 6. The system of claim 5, wherein said main body comprises a gas passage communicating with said first supply hole and a space over said cell.
- 7. The system of claim 5 or 6, wherein said protruded portion comprises a gas passage communicating with said second supply hole and a space over said cell.
- 30 8. The system of any one of claims 5 to 7, wherein said holding member comprises an additional sealing surface against said separator.
 - 9. The system of claim 8, comprising a first sealing member between said sealing surface of said main body and said first main face of said cell, and a second sealing member between said additional sealing surface of said holding member and said separator.
 - 10. The system of any one of claims 5 to 9, wherein a pressure is applied on said first main face in the direction substantially perpendicular to said first main face.
 - 11. The system of any one of claims 5 to 10, comprising a gasket for sealing between said separator and said holding member.
- 50 12. The system of any one of claims 5 to 11, wherein a supply passage communicating with said first supply hole and a space over said cell is formed in said separator.
- 55 13. The system of claim 12, wherein a gas passage communicating with said first supply hole and said space over said cell is not formed in said holding member.

30

40

50

55

said protruded portion is inserted into said through hole.

- 34. The system of claim 33, wherein said main body comprises a gas passage communicating with said first supply hole and a space over said cell.
- 35. The system of claim 33 or 34, wherein said protruded portion comprises a gas passage communicating with said second supply hole and a space over said cell.
- **36.** The system of any one of claims 33 to 35, wherein said holding member comprises an additional sealing surface against said separator.
- 37. The system of claim 36, comprising a first sealing member between said sealing surface of said main body and said first main face of said cell and a second sealing member between said additional sealing surface of said holding member and said separator.
- **38.** The system of any one of claims 33 to 37, wherein a pressure is applied on said first main face in the direction substantially perpendicular to said first main face.
- 39. A connecting member having an electrical conductivity to be contacted with an electrochemical cell, said cell comprising a solid electrolyte film having one and the other surfaces, one electrode provided on said one surface of said film and being to be brought into contact with one gas, and the other electrode provided on the other surface of said film and being to be brought into contact with the other gas, wherein said connecting member comprises a permeable member including an emboss shape-provided portion.
- 40. The member of claim 39, wherein said permeable member has one and the other surfaces, and said emboss shape-provided portion includes a first emboss shape-provided portion protruding on said one face of said permeable member and a second emboss shape-provided portion protruding on the other surface of said permeable member.
- 41. The member of claim 39, wherein said permeable member is composed of a mesh.
- **42.** The member of claim 39, wherein said permeable member is composed of a plate-shaped body with a vent hole formed therein.
- **43.** The member of claim 42, wherein said permeable member is a punching metal or etching metal.

- **44.** The member of claim 42, wherein said permeable member is composed of an expand metal.
- **45.** The member of any one of claims 39 to 44, wherein said one gas is a reducing gas and said connecting member contacts with said one electrode.

Fig. 2

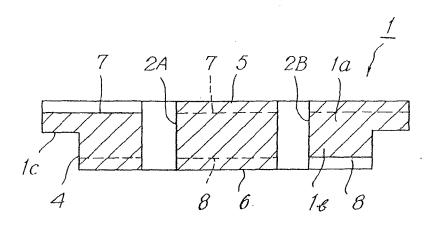
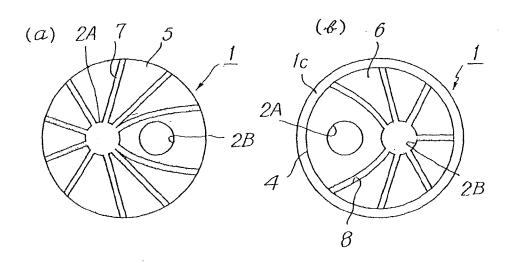


Fig. 3



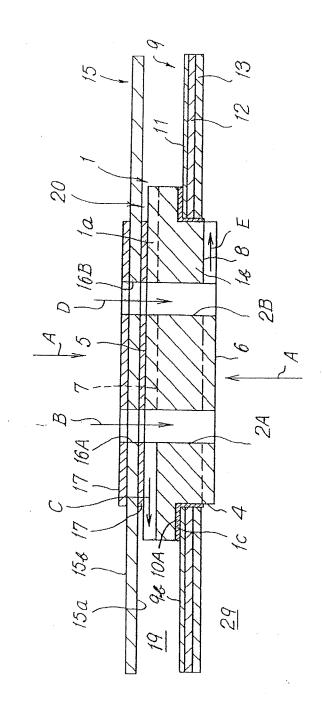


Fig. 5

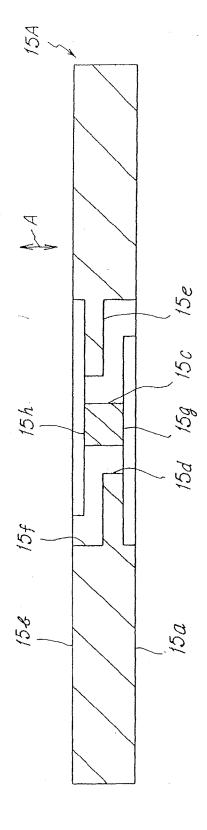
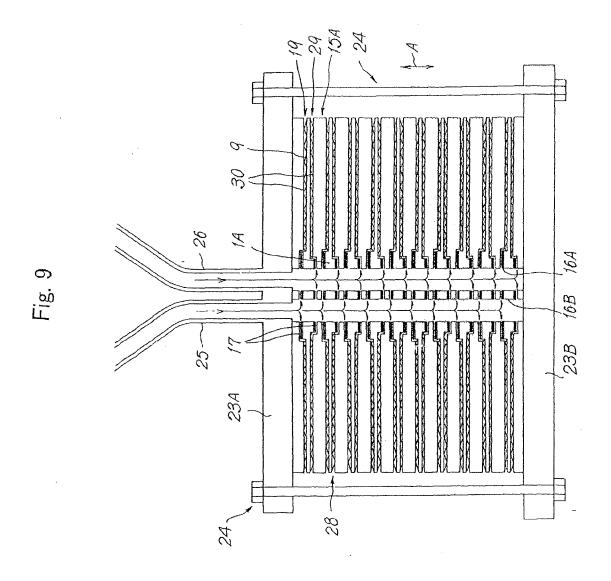


Fig. 7



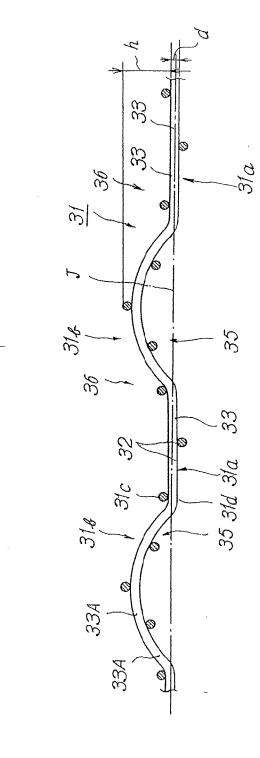


Fig. 1

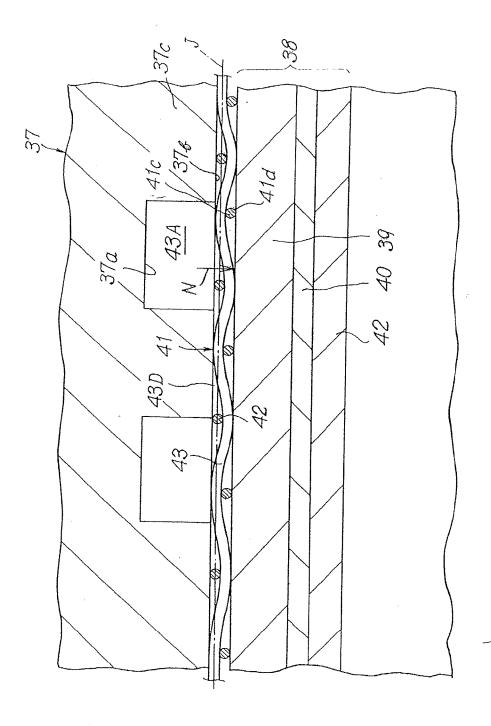


Fig. 1

38 37 43B (B) 354 39 43C 43E 44 33B 51c 33 132 36B ·5/d 516 430 B, 35B **Q**. ××

Fig. 15

Fig. 17

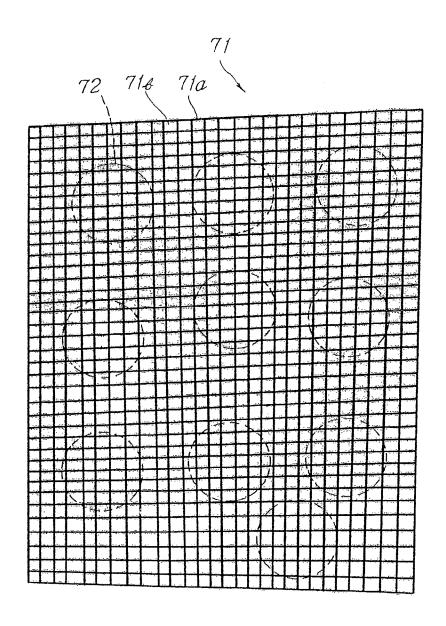
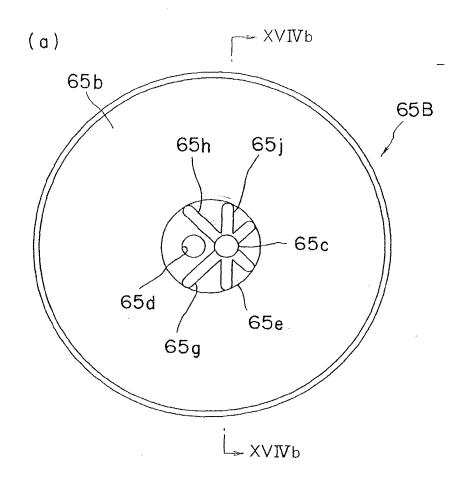


Fig. 19



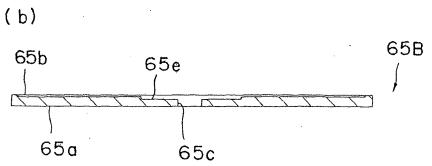
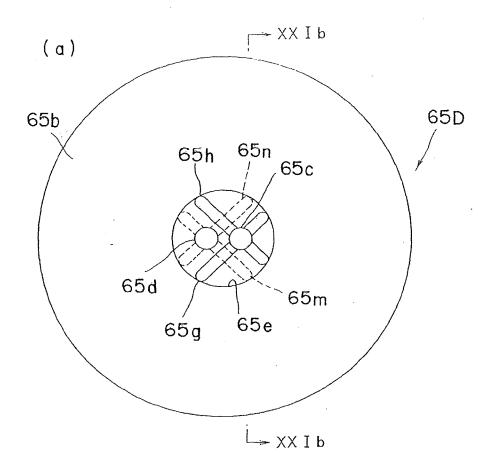


Fig. 21



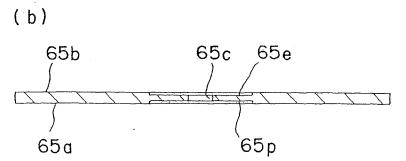
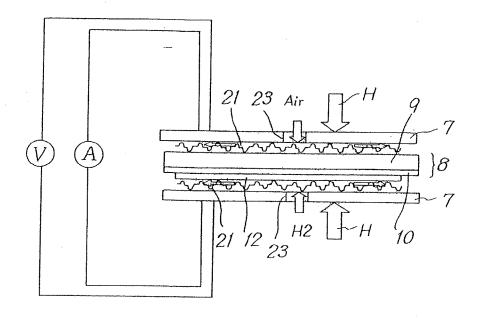


Fig. 23



Europäisches Patentamt

European Patent Office

Office européen des brevets



EP 1 294 035 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3: 08.03.2006 Bulletin 2006/10

(51) Int Cl.: H01M 8/02 (2006.01) H01M 8/24 (2006.01)

(11)

H01M 8/12 (2006.01)

(43) Date of publication A2: 19.03.2003 Bulletin 2003/12

(21) Application number: 02256336.5

(22) Date of filing: 12.09.2002

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR
Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 13.09.2001 JP 2001278076 23.10.2001 JP 2001324603 13.06.2002 JP 2002172368 13.06.2002 JP 2002172673

- (71) Applicant: NGK INSULATORS, LTD. Nagoya-City, Aichi Pref. 467-8530 (JP)
- (72) Inventors:
 Ito, S.,
 Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi,
 Aichi-ken 467-8530 (JP)

- Ryu, T., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)
- Shimizu, S., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)
- Okumura, K., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)
- Hattori, M., Intel. Prop. Dept NGK Insulators Ltd Nagoya-shi, Aichi-ken 467-8530 (JP)
- (74) Representative: Paget, Hugh Charles Edward et al Mewburn Ellis LLP York House
 23 Kingsway London WC2B 6HP (GB)
- (54) A holding member for holding an electrochemical cell, a holding structure for the same, an electrochemical system and a connecting member for electrochemical cells

(57) The invention provides an assembly structure for facilitating the assembly of laminated single cells, for reducing the possibility of gas leakage after repeated cycles of temperature elevation and reduction, and for preventing the reduction of working efficiency of cells due to the gas leakage. A plate-shaped electrochemical cell 9 made of a ceramic material with a through hole 9a formed therein is held by a holding member 1. The member 1 is made of a ceramic material and has a

plate-shaped main body 1a of a shape of a flat plate and a protruded portion 1b protruding from the main body 1a. A first supply hole 2A for supplying one gas and a second supply hole 2B for supplying the other gas are formed in the holding member 1. The main body 1a has a seafing surface 1c against the one main face 9a of the cell 9 while the protruded portion 1b is inserted into the through hole 9a.



EUROPEAN SEARCH REPORT

Application Number EP 02 25 6336

		PERED TO BE RELEVANT	Τ ,		
Category	Gitation of document with i of relevant passa	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)		
Y	MACKELVIE, WINSTON 29 December 1999 (* page 5, line 3 - * page 6, line 25 * page 10, line 8 * figure 10 *	1999-12-29) line 34 * - line 30 * - line 12 * - page 14. line 13 *	1-24 33-38	H01M8/02 H01M8/12 H01M8/24	
A	US 5 212 023 A (DIE 18 May 1993 (1993-(* column 6, line 63		1-24		
A	EP 0 706 229 A (OS/ 10 April 1996 (1996 * column 9, line 12 * figure 2 *	5-04-10)	1-24		
A	US 5 549 983 A (YAM 27 August 1996 (199 * column 3, line 15		1-24	TECHNICAL FIELDS SEARCHED (IPC)	
	EP 0 722 193 A (SUL HEXIS AG) 17 July 1 * the whole documer	ZER INNOTEC AG; SULZER 996 (1996-07-17)	1-24	H01M	
	DE 196 49 456 A1 (S MUENCHEN, DE) 4 Jur * the whole documer	ie 1998 (1998-06-04)	25-32, 39-45 33-38	**	
	DE 195 17 443 A1 (M TURBINEN-UNION FRIE FRIEDRICHS) 14 Nove * the whole documen	25-32, 39-45			
	The present search report has t	-/			
	Place of search	Date of completion of the search	<u> </u>	Evampa	
	The Hague	12 January 2006	C+2	ndaert, F	
X : partic Y : partic docum A : techn O : non-v	TEGORY OF CITED DOCUMENTS sularly relevant if taken alone ularly relevant if combined with anothent of the same category ological background written disclosure nediate document	T : theory or principle E : earlier patent doci after the filing date	underlying the in ument, but publis the application other reasons	ivention hed on, or	

EPO FORM 1503 03.82 (P04C01)



Application Number

EP 02 25 6336

CLAIMS INCURRING FEES
The present European patent application comprised at the time of filing more than ten claims.
Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.
LACK OF UNITY OF INVENTION
The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:
see sheet B
All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 02 25 6336

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-01-2006

	Patent document ted in search report	rt	Publication date		Patent family member(s)		Publication date
WO	9967845	Α	29-12-1999	AU CA	4355399 2241566		10-01-20 23-12-1
US	5212023	A	18-05-1993	CA DE EP JP JP NO	2048710 59108285 0473540 3098813 4306568 913345	D1 A2 B2 A	28-02-1 21-11-1 04-03-1 16-10-2 29-10-1 28-02-1
EP	0706229	А	10-04-1996	DE DE JP JP US	69503014 69503014 3007814 8162141 5549982	T2 B2 A	23-07-1 11-02-1 07-02-2 21-06-1 27-08-1
US	5549983	A	27-08-1996	AU DE DE EP JP WO	1578697 69716401 69716401 0876687 2000506667 9727639	D1 T2 A1 T	20-08-19 21-11-20 26-06-20 11-11-19 30-05-20 31-07-19
EP.	0722193	A	17-07-1996	AT DE DK	191992 59508195 722193	D1	15-05-20 25-05-20 10-07-20
DE	19649456	A1	04-06-1998	NONE			
DE	19517443	A1-	14-11-1996	NONE			
US	5902692	A	11-05-1999	AT AU AU CN DE DK EP JP	303001 720351 4358697 1191398 59611263 0840388 0840388 10134831	B2 A A D1 T3	15-09-20 01-06-20 07-05-19 26-08-19 29-09-20 19-09-20 06-05-19 22-05-19
WO			18-03-1999			T A	19-07-20 02-10-20 29-06-20 03-09-20

FORM P0459

 $\stackrel{\mathrm{C}}{\cong}$ For more details about this annex : see Official Journal of the European Patent Office, No. 12/82